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TITLE: Nanostructured NiFe<sub>2</sub>O<sub>4</sub> Soft Magnetic Ferrite

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### Nanostructured $\text{NiFe}_2\text{O}_4$ Soft Magnetic Ferrite

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**ABSTRACT:**  $\text{NiFe}_2\text{O}_4$  is an important high frequency soft magnetic material due to its ultra high resistivity; however, its initial permeability is rather low. Conventional magnetic ferrites are manufactured through ceramic processing. In an effort to explore innovative approaches for fabricating ferrite materials with improved performance, a study of fabricating nanostructured  $\text{NiFe}_2\text{O}_4$  using wet chemical approaches has been carried out. The synthetic  $\text{NiFe}_2\text{O}_4$  precursor was synthesized by a citrate reaction method followed by calcinating at various temperatures. Systematic studies concerning the crystallographic structure, the nanostructure and morphology of the particle, the phase homogeneity, the conditions for chemical reaction completion, and the magnetic properties have been carried out using x-ray diffraction, transmission electron microscopy, and magnetic measurements. The results show that by using a citrate reaction approach, pure phase and stoichiometric  $\text{NiFe}_2\text{O}_4$  can be fabricated easily, and the particle size can be controlled on a nanometer scale, even at high calcination temperatures. In addition, a comparative study of the  $\text{NiFe}_2\text{O}_4$  fabricated by conventional ceramic processing and this new citrate processing will be presented.

### INTRODUCTION

The development of personal computers and electronic equipment and devices is proceeding in the direction of miniaturization and high frequency operation. With high resistivity, ferrites play a leading role in many high frequency applications such as power electronics, communications, consumer electronics, and microwave equipment. Among the various types of ferrite magnetic materials [1-3],  $\text{NiFe}_2\text{O}_4$  represents one of the best ferrites for ultra high frequency applications.

Since their discovery in the 1940's, ferrites were fabricated via ceramic processing which involved a solid state reaction between the constituent metal oxides at high temperatures. Although there have been a substantial improvement in the properties of conventional ferrites, the progresses are limited and the magnetic properties of the ferrites cannot satisfy the increasing demand for high quality ferrite products. In the request for improved magnetic properties, perhaps the most important task is to develop a novel synthesis approach. Based on this consideration, an aqueous solution reaction technique was developed to synthesis nanophase  $\text{NiFe}_2\text{O}_4$  particles. This report deals with the synthesis of  $\text{NiFe}_2\text{O}_4$ , and its structural and magnetic properties.

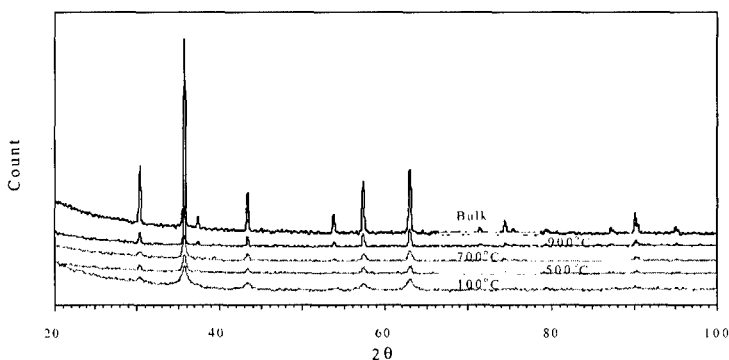
### EXPERIMENTS

Low temperature synthesis approaches based on the aqueous synthesis method have been developed in recent years to synthesis very fine  $\text{NiFe}_2\text{O}_4$  (n- $\text{NiFe}_2\text{O}_4$ ) particles [4-5]. The

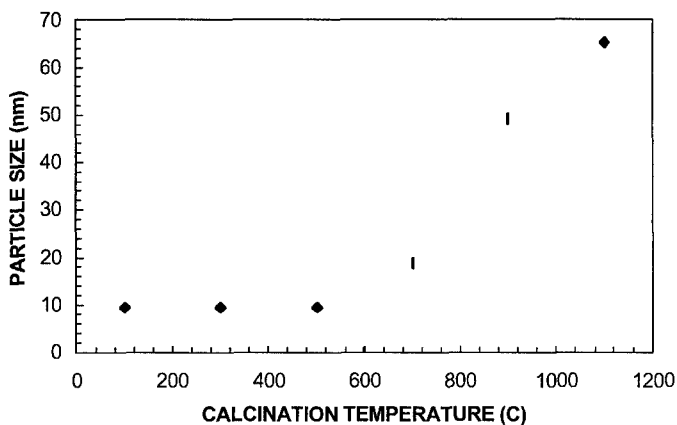
synthesis method used in this work is as follows. The parent materials are iron (III) citrate, nickel nitrate, and citric acid. First, the iron citrate tri-hydrate and the nickel citrate tri-hydrate were dissolved separately in DI water. The two clear solutions were mixed together and slowly dried until the solution was concentrated and became sticky. The concentrated mixture was further dried in an oven at 40 °C for 8 hours. The dried powder was crushed and passed through a 60 mesh screen. The crushed powder was calcined in the temperatures between 100 to 900 °C for 2 hours in a controlled oxygen atmosphere. Characterization of the crystal structure and particle size of the synthetic powders was carried out using x-ray diffraction (XRD) with Cu K $\alpha_1$  radiation. The nanostructure of the NiFe<sub>2</sub>O<sub>4</sub> particle was also examined using high-resolution transmission electron microscopy (HRTEM) and Mossbauer effect (ME) experiments. Static magnetic properties of the synthetic NiFe<sub>2</sub>O<sub>4</sub> nanoparticles were measured using a Quantum Design SQUID magnetometer at temperatures between 10 K and 300K.

## RESULTS AND DISCUSSION

**Structure** Figure 1 shows the XRD pattern for the n-NiFe<sub>2</sub>O<sub>4</sub> powder samples calcined at 100, 500, 700, and 900 °C. For comparison, the figure also includes the XRD pattern of a bulk-size conventional NiFe<sub>2</sub>O<sub>4</sub> powder sample. The x-ray diffraction results identify that all of the synthetic NiFe<sub>2</sub>O<sub>4</sub> powders have the same spinel NiFe<sub>2</sub>O<sub>4</sub> structure. As shown in Figure 1, the linewidths of XRD diffraction peaks for the n-NiFe<sub>2</sub>O<sub>4</sub> are significantly broader than that for the bulk NiFe<sub>2</sub>O<sub>4</sub> sample. From the linewidth of the main peak (at 35.7°), the mean particle size of the NiFe<sub>2</sub>O<sub>4</sub> nanoparticle samples calcined at different temperatures was calculated according to the Scherrer equation [6]. Figure 2 shows the particle size of the synthetic NiFe<sub>2</sub>O<sub>4</sub> nanoparticles as a function of the calcination temperature. It can be seen that when the calcination temperature



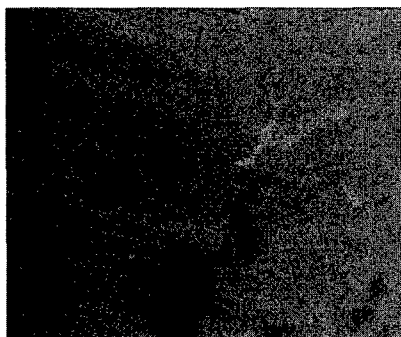
**Figure 1.** XRD pattern for nanostructured NiFe<sub>2</sub>O<sub>4</sub> and micro-sized (bulk) NiFe<sub>2</sub>O<sub>4</sub>



**Figure 2.** The particle size of n-NiFe<sub>2</sub>O<sub>4</sub> as a function of the calcination temperature

is 500 °C or below, the NiFe<sub>2</sub>O<sub>4</sub> particle size remains small (10 nm) with little change with temperature; while beyond 700 °C, the particle size significantly increases with increasing calcination temperature.

High-resolution transmission electron microscopy experiments were carried out to study the nanostructure of the synthetic NiFe<sub>2</sub>O<sub>4</sub> samples. Bright field images, electron diffraction, and lattice images were obtained. A typical HRTEM image showing the morphologies of the NiFe<sub>2</sub>O<sub>4</sub> nanoparticle materials is presented in Figure 3. This image shows many nanoparticles. It is very interesting that several nanoparticles appear for this particular set of lattice fringes, implying that it is possible that the particles do not have a random orientation. Many Moire fringes are distinguished, the array of nanoparticles is 3-D.



**Figure 3.** A typical atomic resolution TEM image showing the morphology of the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles. The bar corresponds to 20 nm.

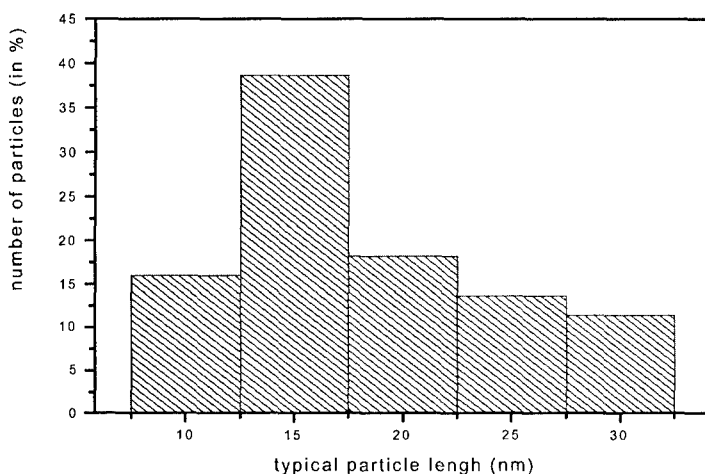


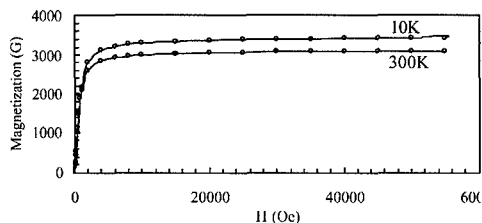
Fig. 4. Particle size distribution of NiFe<sub>2</sub>O<sub>4</sub> obtained by TEM

The image shows a rather dispersive particle size distribution between 10nm and 30 nm. Figure 4 shows the particle size distribution obtained by TEM. The width of the distribution is approximately 25 nm and there is a peak centered around 15 nm. For this histogram, 54 particles were counted and analyzed. The typical length in the figure is an average between the maximum and minimum lateral dimensions measured from the TEM image.

It was found in this study of nanostructured ferrites that the nanostructured ferrite particle may consist of an outer amorphous shell and an inner crystalline core such that the relative shell thickness increases with the reduction in the particle size. To gain some insight into the nanostructure of the synthetic NiFe<sub>2</sub>O<sub>4</sub> nanoparticles, a ME experiment has been carried out on these samples. The results indicate that the NiFe<sub>2</sub>O<sub>4</sub> calcined at low temperatures possess a dominantly amorphous structure. With increasing calcination temperature, the crystalline constituent increases until 700 °C, beyond which, crystalline phase becomes dominant. The details of the ME study will be published elsewhere [7].

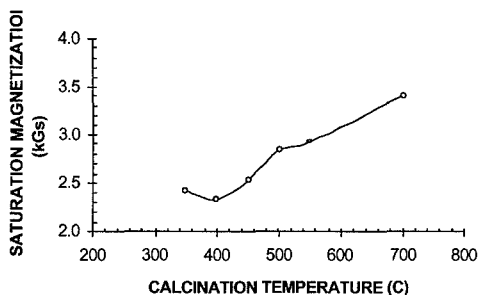
#### **Static magnetic properties of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles**

Figure 5 shows typical magnetization curves measured at 10 K and 300 K for the n-NiFe<sub>2</sub>O<sub>4</sub> powder sample calcined at 700°C. It can be seen from the figure that the magnetization of n-NiFe<sub>2</sub>O<sub>4</sub> is close to saturation for a field of 10 kOe. The saturation magnetization of the powder at 10K is obtained to be 3410G. Figure 6 shows the saturation magnetization as a function of calcination temperature. Starting from 400 °C, calcination at an elevated temperature makes the NiFe<sub>2</sub>O<sub>4</sub> phase more completely formed, thus the saturation magnetization increases with increasing the calcination temperature. For conventional bulk NiFe<sub>2</sub>O<sub>4</sub>, the saturation magnetization at 10 K is 3800 G. As shown in Figure 6, the same value can be reached for the as-synthesized nanosized NiFe<sub>2</sub>O<sub>4</sub> when calcination occurs at 700 °C or higher.

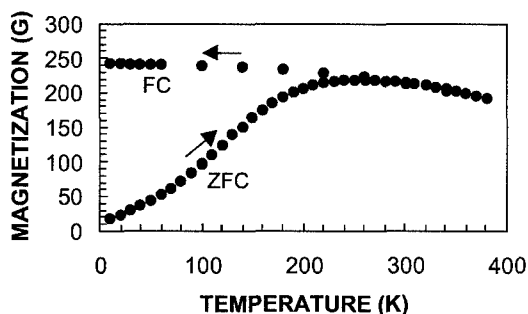


**Figure 5.** Magnetization curves for the 700°C calcined n-NiFe<sub>2</sub>O<sub>4</sub> powder sample measured at 10 K and 300 K.

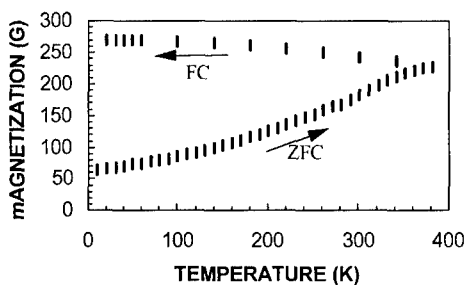
Figure 7 shows the temperature dependence of low field magnetization for the n-NiFe<sub>2</sub>O<sub>4</sub> calcined at 100 °C. In this measurement, the sample was cooled from room temperature to 4.2 K in a zero magnetic field (ZFC), and then a 100 Oe field was applied. The magnetization on the 700 °C calcined sample; the result is shown in Figure 8. As can be seen from the figure, the monotonic increase of the magnetization with increasing temperature and the complete irreversible change of magnetization when reducing the temperature clearly prove that the particle size is larger for the 700 °C calcined sample.



**Figure 6.** The variation of saturation magnetization measured at 10 K with calcination temperature for nanostructured NiFe<sub>2</sub>O<sub>4</sub>.



**Figure 7.** Magnetization in a field of 100 Oe as a function of temperature for the 100 °C calcined n-NiFe<sub>2</sub>O<sub>4</sub> powder sample. The arrows indicate the direction of the temperature variation.



**Figure 8.** Magnetization as a function of temperature for the 700 °C calcined n-NiFe<sub>2</sub>O<sub>4</sub> powder sample. The arrows indicate the direction of the temperature variation.

## CONCLUSIONS

Based on the structural and magnetic properties, it is determined that the synthetic nanostructured NiFe<sub>2</sub>O<sub>4</sub> possesses high phase purity and controllable particle size. By calcining at 700°C, the synthetic NiFe<sub>2</sub>O<sub>4</sub> nanoparticle possesses a saturation magnetization of 3841Gs and a particle size of about 20 nm. These characteristics are favorable for fabricating a nanophase NiFe<sub>2</sub>O<sub>4</sub> ferrite.

## ACKNOWLEDGMENTS

The work at Inframat Corporation is supported by US Air Force Contract No. F29601 01-C-0141.

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